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(54) DIRECT HAIR DYEING COMPOSITION, CONTAINING A CROSSLINKED
POLYMER WITH ACRYLIC AND C₁₀-C₃₀ ALKYL ACRYLATE UNITS

(57) The invention concerns a hair dyeing composition, containing at least one direct dye, characterized by the fact that it also contains a crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units. The invention also concerns the use of a crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units in or for production of a hair dyeing composition, containing at least one direct dye, to improve the dyeing capacity of said composition, especially after storage at about 10°C, and especially at about 4°C.

Another purpose of the invention is a process for preservation of dyeing capacity, especially after storage at a temperature lower than about 10°C, of a dyeing composition, containing at least one direct dye, characterized by the fact that an effective amount of said crosslinked polymer is added to the composition.

The invention concerns a hair dyeing composition, containing at least one direct dye and at least one crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units.

It is known that hair fibers can be dyed with direct dyeing compositions according to a so-called "direct coloration" process, which consists of applying to the fibers dye molecules having affinity for said fibers and allowing them to stand, and then rinsing the fibers. The resulting colorations are temporary or semi-permanent colorations, depending on the nature of the interactions between the direct dyes and the hair fiber and their desorption from the surface and/or core of the fiber.

To facilitate application of such dyeing compositions to the hair, in particular, to avoid their flowing onto the forehead and face or beyond the initially chosen point of application during application or during the pause necessary for coloration, one conventionally increases the viscosity of the compositions with crosslinked polyacrylic acid (thickener).

However, dyeing compositions based on direct dyes and crosslinked polyacrylic acids have not proved to be sufficiently satisfactory in terms of their dyeing properties after having been stored for a certain time at a lower temperature than ambient temperature, for example, below 10°C, and especially about 4°C.

It is thus observed that compositions stored under such conditions produce a weaker absorption of the direct dye on the hair and therefore present insufficient dyeing capacity.

The present invention seeks to solve the aforementioned problem, i.e., to propose a means that permits preservation of the dyeing capacity of dyeing compositions containing a direct dye, capable of being stored at low temperatures, especially at temperatures lower than 10°C.

Hence, after numerous investigations conducted on this question, the applicant has just discovered that it is possible to preserve the dyeing capacity of direct dye compositions, if an effective amount of a crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units is added to these compositions.

Even after more or less prolonged storage at temperatures below 10°C, especially close to 4°C, compositions are obtained with good dyeing capacity, and whose absorption on the hair is very satisfactory.

This discovery is the basis of the present invention.

The purpose of the present invention is therefore a cosmetic hair dyeing composition of the type containing, in a cosmetically acceptable support appropriate for dyeing, at least one direct dye, and characterized by the fact that it also contains at least one crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units.

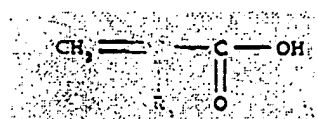
Another purpose of the present invention is the use of a crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units in or for production of a direct dyeing composition for hair, containing at least one direct dye, to improve preservation of the dyeing capacity of said composition, especially after storage at about 10°C, and especially at about 4°C.

The invention also concerns a process for improving preservation of the dyeing capacity, in particular, after storage below about 10°C, and especially about 4°C, of a dyeing composition for hair, containing at least one direct dye, which consists of introducing to said composition of an effective amount of at least one crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units.

It finally concerns a hair dyeing process employing the compositions with improved properties according to the invention.

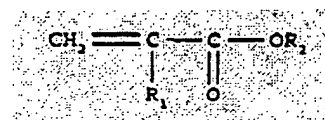
But other characteristics, aspects, objects and advantages of the invention will be more readily apparent on reading the following description and example.

According to the invention, acrylic units are understood to mean units of the structure



in which R₁ denotes H or CH₃ or C₂H₅, i.e., acrylic, methacrylic acid or ethacrylic acid units.

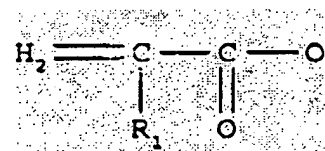
Alkyl acrylate units are also understood to mean units of the structure



in which R₁ denotes H or CH₃ or C₂H₅, i.e., acrylate, methacrylate or ethacrylate units, R₂ denoting a C₁₀-C₃₀ alkyl radical, preferably C₁₂-C₂₂.

The crosslinked polymer or polymers with acrylic units and C₁₀-C₃₀ alkyl acrylate units, usable in the context of the present invention, can denote more particularly a terpolymer of a mixture of monomers containing essentially:

- (a) an acrylic, methacrylic or ethacrylic acid, but preferably acrylic or methacrylic acid,
- (b) an acrylate with the formula:



in which R₁ denotes H or CH₃ or C₂H₅, but preferably H or CH₃, and R₂ denotes an alkyl radical having 10 to 30 carbon atoms, and preferably 12 to 22 carbon atoms, and

- (c) a crosslinking, polymerizable monomer containing a //insert// with at least one other polymerizable group, whose unsaturated bonds are not conjugated relative to each other.

Acrylates according to the invention include, for example, lauryl acrylate, stearyl acrylate, decyl acrylate, isodecyl acrylate, dodecyl acrylate and the corresponding methacrylates, lauryl methacrylate, stearyl methacrylate, decyl methacrylate, isodecyl methacrylate and dodecyl methacrylate.

The crosslinking polymerizable monomers of type (c) include, for example, and preferably, polyallyl ethers, like, polyallyl sucrose and polyallyl pentaerythritol.

The crosslinked polymers of this type are well known: they are prepared and described in Patents US-3 915 921 and 4 505 949.

According to the invention, one can use, in particular, (i) those consisting of 95 to 60 wt.% acrylic units, 4 to 40 wt.% acrylate units and 0.1 to 6 wt.% crosslinking monomer type (c), or (ii) those consisting of 98 to 96 wt.% acrylic units, 1 to 4 wt.% acrylate units and 0.1 to 0.6 wt.% crosslinking monomer of type (c).

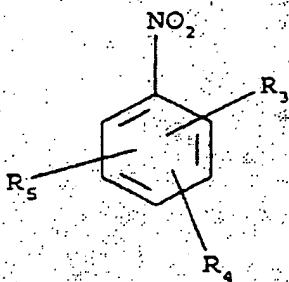
Among the aforementioned crosslinked polymers, the products marketed by the GOODRICH company under the commercial names PEMULEN TR1, PEMULEN TR2, CARBOPOL 1342, and preferably PEMULEN TR1, are particularly preferred according to the present invention.

The crosslinked polymers with acrylic units and C₁₀-C₃₀ alkyl acrylate units described above are used in the dyeing composition according to the invention in proportions that can range from about 0.05 to about 5%, and preferably about 0.1 to about 3% by weight, relative to the total weight of the composition.

The direct dyes usable in the dyeing composition according to the present invention are direct dyes in the aforementioned sense, i.e., usable according to a conventional direct dyeing process. Among those conventionally used, one can cite the nitrobenzene dyes, like, nitrophenylenediamines, nitrodiphenylamines, nitroanilines, nitrophenol ethers or nitrophenols, nitropyridines, anthraquinone dyes, mono- or diazo dyes, triarylmethane dyes, azine dyes, acridine dyes and xanthene dyes, or even metalliferous dyes.

The more particularly preferred direct dyes according to the invention are chosen among the following:

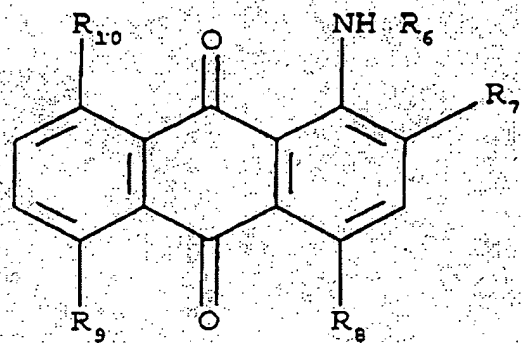
i) the nitrobenzene dyes of the following formula (I):



in which:

- R_3 denotes an NH_2 radical, amino monosubstituted with an alkyl, monohydroxyalkyl, polyhydroxyalkyl, aminoalkyl radical or amino disubstituted with identical or different alkyl, mono- or polyhydroxyalkyl or aminoalkyl radicals,
- R_4 denotes hydrogen, hydroxy, alkoxy, mono- or polyhydroxyalkyloxy, or the same meanings mentioned above for R_3 , except for the disubstituted amino radical,
- R_5 denotes hydrogen, alkyl, nitro or halogen,

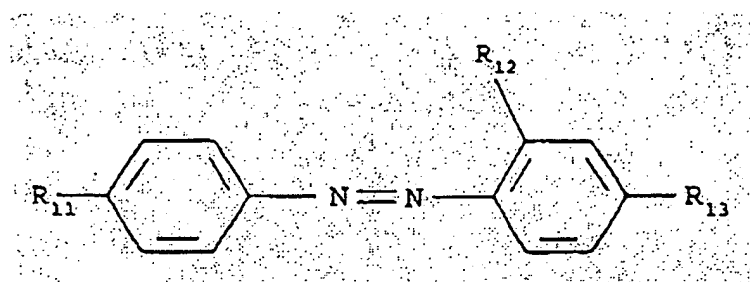
ii) anthroquinone dyes of the following formula (II):



in which

- R_6 denotes hydrogen, a monohydroxyalkyl or polyhydroxyalkyl radical,
- R_7 denotes hydrogen, an alkyl or alkoxy radical,
- R_8 denotes hydrogen, a hydroxy, amino or monohydroxyalkylamino or polyhydroxyalkylamino radical,
- R_9 and R_{10} , identical or different, are hydrogen, hydroxy or amino,

iii) azo dyes of the following formula (III):



in which:

- R₁₁ denotes a nitro, amino, mono- or disubstituted amino with alkyl,
- R₁₂ denotes hydrogen or an alkyl radical,
- R₁₃ denotes an amino, mono- or disubstituted amino with monohydroxyalkyl,

it being understood that the aforementioned alkyl and alkoxy radicals in formulas (I), (II) and (III) are C₁-C₄ and they can be linear or branched, and the cosmetically acceptable salts of all these compounds.

C₁-C₄ is understood, in particular, to mean the methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl and tert-butyl radicals.

Cosmetically acceptable salts denote, in particular, the hydrochlorides, hydrobromides and sulfates.

Even more advantageously, according to the present invention, use of the following direct dyes is preferred:

- 1-amino-2-nitro-4-N-(β-hydroxyethyl)amino-5-methylbenzene,
- 1,4,5,8-tetraaminoanthraquinone,
- 1,4-bis-N,N'-[(β,γ-dihydroxypropyl)amino]anthraquinone,
- 1,4,4-N-tris-(β-hydroxyethyl)-1,4-diamino-2-nitrobenzene,
- 1-N-(β-hydroxyethyl)amino-2-nitro-4-aminobenzene,
- 1-hydroxy-3-nitro-4-aminobenzene,
- 1-hydroxy-3-nitro-4-N-(β-hydroxyethyl)aminobenzene,
- 1-β-hydroxyethyloxy-3-methylamino-4-nitrobenzene,
- 1-methylamino-2-nitro-5-β,γ-dihydroxypropyloxybenzene,

- 1-N-(β -aminoethyl)amino-2-nitro-4- β -hydroxyethoxybenzene,
 - 4-[N-ethyl-N-(β -hydroxyethyl)amino]-1-N-(β -hydroxyethyl)amino-2-nitrobenzene,
 - 1-(4'-aminodiphenylazo)-2-methyl-4-N-bis-(β -hydroxyethyl)aminobenzene,
 - 1-methoxy-3-N-(β -aminoethyl)amino-4-nitrobenzene,
 - 1-amino-2-nitro-4-N-(β -hydroxyethyl)aminobenzene,
 - 1-amino-2-nitro-4-N-bis-(β -hydroxyethyl)aminobenzene,
 - 1,4-N-bis-(β -hydroxyethyl)amino-2-nitrobenzene,
 - 1-amino-2-N-(β -hydroxyethyl)amino-5-nitrobenzene,
 - 1,4-diaminoanthraquinone,
- and their cosmetically acceptable salts.

These direct dyes, in the form of a base or salt, are generally present in the dyeing composition according to the invention in amounts ranging from about 0.001 to about 10%, and preferably from about 0.05 to about 5% by weight, relative to the total weight of the composition.

The cosmetically acceptable medium for dyeing is an aqueous medium that can contain one or more organic solvents chosen, for example, among ethyl alcohol, isopropyl alcohol, benzyl alcohol and phenylethyl alcohol, or glycols or glycol ethers, like, propylene glycol or its ethers, like, propylene glycol monomethyl ether, butylene glycol monomethyl ether, dipropylene glycol monomethyl ether, monomethyl, monoethyl and monobutyl ethers of ethylene glycol, as well as diethylene glycol alkyl ethers, like, diethylene glycol monoethyl ether or monobutyl ether, in amounts between about 0.5 and 20%, and preferably between about 2 and 10% by weight, relative to the total weight of the composition.

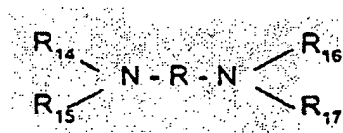
Aliphatic amides, like the mono- and diethanolamides of acids derived from copra, lauric acid or oleic acid, at concentrations between about 0.05 and 10 wt.%, can also be added to the composition according to the invention.

Surfactants well known in the prior art and of the anionic, cationic, nonionic, amphoteric, zwitterionic type or their mixtures can also be added to the composition according to the invention, preferably in an amount between about 0.1 and 50 wt.%, and advantageously between about 1 and 20 wt.%, relative to the total weight of the composition.

Said dyeing composition can also contain various common adjuvants, like, antioxidants, perfumes, sequestering agents, dispersants, hair conditioning agents, preservatives, opacifiers, as well as any other adjuvant ordinarily used in hair dyeing.

Naturally, one skilled in the art will make sure to choose the complementary compound or compounds mentioned above so that the advantageous properties intrinsically connected to the dyeing composition according to the invention are not altered by the contemplated additive or additives, or not substantially so.

The dyeing composition according to the invention can be formulated at acid, neutral or alkaline pH, and the pH can vary from 3 to 12, and preferably from 7 to 11, and most preferably from 8.5 to 10, and can be adjusted by means of alkalization or acidification agents already known. As alkalizing agents, one can cite ammonia, alkali carbonates, alkanolamines, for example, mono-, di- and triethanolamines and their derivatives, sodium or potassium hydroxides and compounds of the formula:



in which R is a propylene group optionally substituted with a hydroxyl group or C₁-C₄ alkyl radical; R₁₄, R₁₅, R₁₆ and R₁₇, simultaneously or independently of each other, represent a hydrogen atom, a C₁-C₄ alkyl radical or C₁-C₄ hydroxyalkyl radical.

The acidifying agents are conventionally mineral or organic acids, like hydrochloric, tartaric, citric and phosphoric acids.

The composition applied to the hair can be present in various forms, such as in the form of liquid, cream, gel or any other appropriate form, to accomplish hair dyeing. In particular, it can be packaged under pressure in an aerosol container in the presence of a propellant and form a foam.

Another object of the present invention concerns a process for hair dyeing by direct coloration, consisting of applying to dry or wet hair a dyeing composition as defined above, then allowing said composition to act, preferably for about 3 to 60 minutes, rinsing the hair and optionally washing it, and then rinsing it again and drying it.

One can also allow the composition to act and then dry it.

Specific examples illustrating the invention will now be provided.

EXAMPLE 1:

The following dyeing composition is prepared:

Direct dye (1)*			0.1 g
Ethoxylated decyl alcohol with 5.3 mol ethylene oxide			2.0 g
Lauric acid			1.0 g
Diethylene glycol monobutyl ether			5.0 g
PEMULEN TR1 from Good rich (crosslinked acrylic acid /			
C ₁₀ -C ₃₀ alkyl acrylate copolymer)			0.51 g
2-amino-2-methyl-1-propanol	q.s.	pH	9.5
Demineralized water	q.s.p.		100 g

*direct dye (1): 1-amino-2-nitro-4-N-(β -hydroxyethyl)amino-5-methylbenzene.

After 24 hours, the viscosity of this composition is measured with a Contrave viscosimeter at 25°C. The recorded viscosity is 200 cp.

This composition was then applied to locks of natural gray hair with 90% white, and the composition allowed to sit for 30 minutes. The locks were then rinsed with running water and dried.

The locks were dyed in a nuance expressed in the MUNSSELL value (ASTM Standard D 1535-68, which defines the color: H, denoting the nuance or hue, V, denoting the intensity or value and C, denoting the purity or chromaticity), on a MINOTA CM 2002 colorimeter, as follows: in H, V, C.: 7.5 R 4.7 / 2.9.

The control locks (undyed) had an H, V, C nuance: 3.8 Y, 5.7 / 1.6.

The composition prepared above was also stored for 1 month at a temperature of 4°C.

The composition so stored was then applied to locks of hair of the same quality and according to the same method as above.

The nuance of the locks dyed with this composition stored at 4°C was as follows:

in H, V, C: 7.9 R 4.7 / 2.8.

The color modification between the locks dyed with the initial composition and those dyed with the composition stored for 1 month at a temperature of 4°C was then quantified, using the NICKERSON equation, which defines the color variation indices:

$I = (C/5) \times 2\Delta H + 6\Delta V + 3\Delta C$ (this equation is described in the publication: "Journal of the Optical Society of America", 1944 September, Vol. 34, No. 9, pages 550-570).

Thus, the modification of coloration I_b (index of color variation between the locks dyed with the composition stored for 1 month at a temperature 4°C and that of the locks dyed with the initial composition) referred to the initial coloration I_a (color variation index of the locks dyed with the initial composition and that of the control locks), expressed in %, was 3.7%.

COMPARATIVE EXAMPLE 2:

A dyeing composition similar to that of example 1 was prepared, with a viscosity equal to that of example 1, based on a polymer of the prior art, merely replacing the 0.51 g of PEMULEN TR1 with 0.57 g of CARBOPOL 980 from the Goodrich company (crosslinked polyacrylic acid of the prior art – MW 4 000 000).

Locks of natural hair with 90% white were dyed with the initial composition (i.e., before storage) and according to a method identical to that of example 1 to a nuance expressed in H, V, C equal to: 8.1 R 4.9 / 2.9. Locks of natural hair with 90% white were dyed with the same composition, but stored for 1 month at 4°C. The obtained nuance was:

H, V, C: 8.7 R 4.8 / 2.8.

The ratio I_b / I_a applied to this example, expressed in %, was 8.5%.

Conclusion:

After storage for 1 month at 4°C, the dyeing composition of example 1, containing a crosslinked polymer according to the present invention, presents a much greater dyeing capacity than that of the dyeing composition of example 2, containing a crosslinked polymer of the prior art, since the degradation expressed by the ratio I_b / I_a , in %, is only 3.7% in the case of example 1, whereas it is 8.5% in the case of example 2.

EXAMPLE 3:

The following dyeing composition was prepared:

Direct dye (2)*			0.1 g
Ethoxylated decyl alcohol with 5.3 mol ethylene oxide			2.0 g
Lauric acid			1.0 g
Diethylene glycol monobutyl ether			5.0 g
PEMULEN TR1 from Good rich (crosslinked acrylic acid /			
C ₁₀ -C ₃₀ alkyl acrylate copolymer)			0.54 g
2-amino-2-methyl-1-propanol	q.s.	pH	9.5
Demineralized water	q.s.p.		100 g

*direct dye (2): 1,4,5,8-tetraaminoanthraquinone (30% dispersed on lignosulfate).

After 24 hours, the viscosity of this composition was measured in a Contrave viscosimeter at 25°C. The recorded viscosity was 220 cp.

This composition was then applied to locks of permed gray hair with 90% white, and the composition allowed to sit for 30 minutes. The locks were then rinsed with running water and dried.

The locks were dyed in a nuance, expressed in a MUNSELL value as follows, in H, V, C: 4.8 B 4.2 / 2.4.

The control locks (undyed) had an H, V, C nuance: 4.4 Y 5.9 / 1.6.

Said composition was then stored for 1 month at a temperature of 4°C.

The composition so stored was then applied to locks of hair of the same quality and according to the same method as above.

The nuance of the locks dyed with this composition stored at 4°C was as follows in H, V, C: 2.1 B 4.4 / 2.2.

The ratio I_b (color variation index between the locks dyed with the compositions stored for 1 month at a temperature of 4°C and that of the locks dyed with the initial composition) to I_a (color variation index between the locks dyed with the initial composition and that of the control locks), expressed in %, was 9.8%.

COMPARATIVE EXAMPLE 4:

A dyeing composition similar to that of example 3 was prepared, with a viscosity equal to that of example 3, based on the polymer of the prior art, merely replacing the 0.55 g of PEMULIN TR1 with 0.57 g of CARBOPOL 2984 from the Goodrich company (crosslinked polyacrylic acid of the prior art – MW 3 000 000).

Locks of permed hair with 90% white were dyed with the initial composition (i.e., before storage) and according to a method identical to that of example 3, to a nuance expressed in H, V, C equal to: 5.4 B 4.1 / 3.1.

Locks of permed hair with 90% white were dyed by means of the same composition, but stored for 1 month at 4°C. The obtained nuance was equal in H, V, C to: 1.6 B 4.3 / 1.9.

The ratio I_b / I_a applied to this example, in %, was 22.9%.

Conclusion:

After storage for 1 month at 4°C, the dyeing composition of example 3, containing a crosslinked polymer according to present the invention, presents a dyeing capacity much greater than that of the dyeing composition of example 4, containing a crosslinked polymer of the prior art, since the degradation expressed by the ration I_b / I_a , in %, is only 9.8% in the case of example 3, whereas it is 22.9% in the case of example 4.

EXAMPLE 5:

The following dyeing composition was prepared:

Direct dye (3)*			0.15 g
Ethoxylated decyl alcohol with 5.3 mol ethylene oxide			2.0 g
Lauric acid			1.0 g
Diethylene glycol monobutyl ether			5.0 g
PEMULEN TR1 from Good rich (crosslinked acrylic acid / C ₁₀ -C ₃₀ alkyl acrylate copolymer)			0.52 g
2-amino-2-methyl-1-propanol	q.s.	pH	9.5
Demineralized water	q.s.p.		100 g

* direct die (3): 1,4-bis-N,N'-[(β,γ -dihydroxypropyl)amino]anthraquinone.

After 24 hours, the viscosity of this composition was measured with a Contrave viscosimeter at 25°C. The recorded viscosity was 210 cp.

This composition was then applied to locks of natural gray hair with 90% white and the composition allowed to stand for 30 minutes. The locks were then rinsed with running water and dried.

The locks were dyed to a nuance expressed in the MUNSELL value in H, V, C as follows: 5.9 GY 5.1 / 1.0.

The control locks (undyed) had an H, V, C nuance: 3.8 Y 5.7 / 1.6.

The above composition was then stored for 1 month at a temperature of 4°C.

The composition so stored was then applied to locks of hair of the same quality and according to the same method as above.

The nuance of the locks dyed with this composition stored at 4°C was as follows in H, V, C: 1.2 GY 5.1 / 1.1.

The ratio I_b (color variation index between the locks dyed with the composition stored for 1 month at a temperature of 4°C and that of the locks dyed with the initial composition) to I_a (color variation index between the locks dyed with the initial composition and that of the control locks), in %, was 16.6%.

COMPARATIVE EXAMPLE 6:

A dyeing composition similar to that of example 5 was prepared, with a viscosity equal to that of example 5, based on a polymer of the prior art, merely replacing the 0.52 g of PEMULEN TR1 with 0.65 g of CARBOPOL 2984 from the Goodrich company (crosslinked polyacrylic acid of the prior art).

Locks of natural hair with 90% white were dyed with the initial composition (i.e., before storage) and according to a method identical to that of example 5, to a nuance expressed in H, V, C equal to: 6.6 GY 5.2 / 1.0.

Locks of natural hair with 90% white were dyed with the same composition, but stored for 1 month at 4°C. The obtained nuance was equal in H, V, C to: 10.0 Y 5.4 / 1.2.

The ration I_b / I_a applied for this example, in %, was 34.2%.

Conclusion:

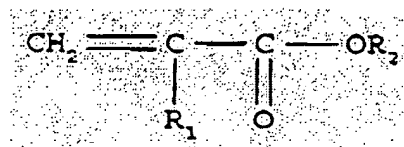
After storage for 1 month at 4°C, the dyeing composition of example 5, containing a crosslinked polymer according to the present invention, presents a much greater dyeing capacity than that of the dyeing composition of example 6, containing a crosslinked polymer of the prior art, since the degradation expressed by the ratio I_b / I_a , in %, was only 16.6% in the case of example 5, whereas it was 34.2% in the case of example 6.

CLAIMS

1. Hair dyeing composition of the type containing, in a cosmetically acceptable support appropriate for dyeing, at least one direct dye, characterized by the fact that it also contains at least one crosslinked polymer with acrylic units and C₁₀-C₃₀ alkyl acrylate units.

2. Dyeing composition according to Claim 1, characterized by the fact the crosslinked polymer is a terpolymer from a mixture of monomers essentially containing:

- (a) an acrylic, methacrylic or ethacrylic acid, preferably acrylic or methacrylic acid,
- (b) an acrylate with the formula:



in which R₁ denotes H or CH₃ or C₂H₅, preferably H or CH₃, and R₂ denotes an alkyl radical having 10 to 30 carbon atoms, and

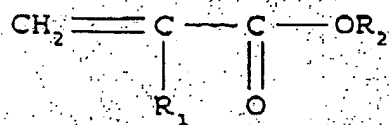
(c) a crosslinking, polymerizable monomer containing a $\text{CH}_2 = \text{C} \begin{array}{l} \diagup \\ \diagdown \end{array}$ group with at least one other polymerizable group, whose unsaturated bonds are not conjugated with each other.

3. Composition according to Claims 1 or 2, characterized by the fact that the alkyl radical of the acrylate unit is C₁₂-C₂₂.

4. Composition according to Claims 1, 2 or 3, characterized by the fact that the crosslinking agent is a polyallyl ether.

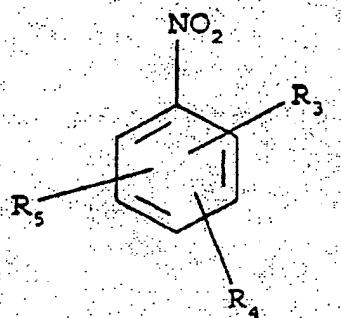
5. Composition according to Claims 1 to 4, characterized by the fact that the crosslinked polymer is a terpolymer of a mixture of monomers containing essentially:

- (a) an acrylic acid,
- (b) an acrylate with the formula:



in which R₁ denotes H or CH₃ and R₂ denotes an alkyl radical having 12 to 22 carbon atoms, and
(c) a polyallyl ether.

6. Composition according to any of the preceding claims, characterized by the fact that the direct dye is a nitrobenzene dye of the following formula (I):

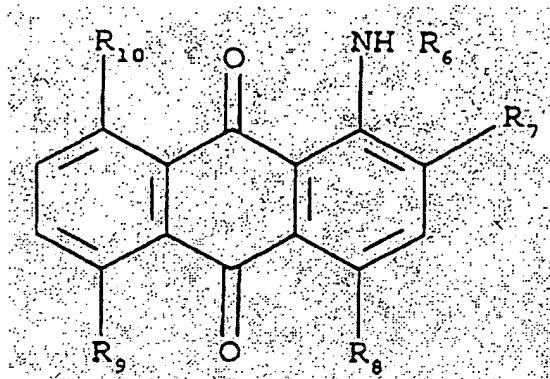


in which:

- R₃ denotes an NH₂ radical, monosubstituted amino with an alkyl, monohydroxyalkyl, polyhydroxyalkyl, aminoalkyl radical or amino disubstituted with identical or different alkyl, mono- or polyhydroxyalkyl or aminoalkyl radicals,
- R₄ denotes hydrogen, hydroxy, alkoxy, mono- or polyhydroxyalkoxy, or the same meanings given above for R₃, except for the disubstituted amino radical,
- R₅ denotes hydrogen, alkyl, nitro or halogen,

it being understood that the aforementioned alkyl and alkoxy radicals are C₁-C₄, and that they can be linear or branched,
and cosmetically acceptable salts of these compounds.

7. Composition according to Claims 1 to 5, characterized by the fact that the direct dye is an anthraquinone dye of the following formula (II):



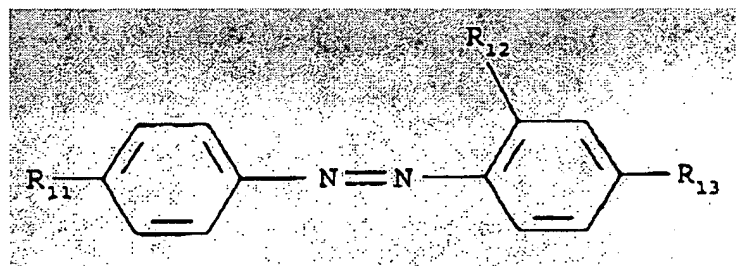
in which

- R_6 denotes hydrogen, a monohydroxy alkyl or polyhydroxyalkyl radical,
- R_7 denotes hydrogen, an alkyl or alkoxy radical,
- R_8 denotes hydrogen, a hydroxy, amino or monohydroxyalkylamino or polyhydroxyalkylamino radical,
- R_9 and R_{10} , identical or different, are hydrogen, hydroxy or amino,

it being understood that the alkyl and alkoxy radicals mentioned above are C_1 - C_4 , and that they can be linear or branched, and cosmetically acceptable salts of these compounds.

8. Composition according to Claim 7, characterized by the fact that the direct anthraquinone dye is 1,4-bis-N,N'-[(β , γ -dihydroxypropyl)amino]anthraquinone.

9. Composition according to Claims 1 to 5, characterized by the fact that the direct dye is an azo dye of following formula (III):



in which:

- R_{11} denotes a nitro radical, amino, mono- or disubstituted amino with alkyl,
- R_{12} denotes hydrogen or an alkyl radical,
- R_{13} denotes an amino radical, or an amino radical mono- or disubstituted with monohydroxyalkyls,

it being understood that the alkyl and alkoxy radicals mentioned above are C₁-C₄, and that they can be linear or branched, and cosmetically acceptable salts of these compounds.

10. Composition according to Claims 6 to 9, characterized by the fact that the cosmetically acceptable salts are hydrochlorides, hydrobromides and sulfates.

11. Composition according to any of the preceding claims, characterized by the fact that the crosslinked polymer is present in amounts ranging from 0.05 to 5 wt. %, relative to the total weight of the composition, and preferably from 0.1 to 3%.

12. Composition according to any of the preceding claims, characterized by the fact that the direct dye is present in the form of a base or salt in amounts ranging from 0.001 to 10 wt.%, relative to the total weight of the composition, and preferably 0.05 to 5%.

13. Composition according to any of the preceding claims, characterized by the fact that the cosmetically acceptable support appropriate for dyeing is an aqueous support, consisting of water and/or organic solvents chosen among alcohols, glycols and glycol ethers in amounts between 0.5 and 20 wt.%, relative to the total weight of the composition.

14. Use of a crosslinked polymer, as defined in any of the Claims 1 to 5, in or for preparation of a direct dyeing composition for hair, containing at least one direct dye, to improve preservation of dyeing capacity of said composition, especially after storage at low temperatures.

15. Process for improving preservation of dyeing capacity, especially after storage at low temperatures, of a dyeing composition containing at least one direct dye, characterized by the fact that an effective amount of a crosslinked polymer, as defined in any of the Claims 1 to 5, is added to said composition.

16. Hair dyeing process by direct coloration, characterized by the fact that a dyeing composition, as defined in any of the Claims 1 to 13, is applied to dry or wet hair, the

composition is allowed to act, the hair is rinsed and then optionally washed, and rinsed again, and finally dried.

17. Hair dyeing process by direct coloration, characterized by the fact that a dyeing composition, as defined in any of the Claims 1 to 13, is applied to dry or wet hair, the composition allowed to act, and then the hair dried.

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INDUSTRIAL

National Registration No.:

PROPERTY OFFICE

RESEARCH REPORT

FA 529726

The present research report was prepared for all patent claims FR 9606430

RELEVANT DOCUMENTS			
Category	Citation of document with indication to the extent possible of the relevant passages	Relates to Claim	
A	FR 2 234 277 A (OREAL) January 17, 1975 *entire document*	1	
A	FR 2 189 380 A (OREAL) January 25, 1974 *entire document*	1	
A	FR 2 382 232 A (OREAL) September 29, 1978 *entire document*	1	
			SUBJECT AREAS RESEARCHED (Int. Cl.6)
			A61K
Date research completed March 12, 1997			Authorized officer Couckuyt, P.
CATEGORY OF CITED DOCUMENTS			
X: of particular interest of itself		T: theories or principles underlying the invention	
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